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(54) SEPARATOR FOR ALKALINE BATTERY AND MANUFACTURE THEREFOR

(57)Abstract:

PROBLEM TO BE SOLVED: To secure high electrolyte retainability, improve the service life of a battery, and prevent interruption of work by cutting by realizing high strength by sulfonating nonwoven fabric, and forming easily sulfonating fiber of continuous fiber.

SOLUTION: Fiber diameter of easily sulfonating fiber is desirably 0.3 to 10 μm, the easily sulfonating fiber is fiber not less than one selected from a group of polystyrene fiber, polyvinyl naphthalene fiber, polyeter sulfone fiber or polycarbonate fiber, the easily sulfonating fiber is syndiotactic polystyrene, at least 20 wt.% of polyolefine fiber is thermally fusible fiber having a fiber diameter not less than 8 μm and the thermally fusible fiber not less than 8 μm, is composite fiber of polypropylene and polyethylene. Therefore, nonuniformity of Metsuke unit (weight unit area) of a separator is reduced, and uniformity is improved to prevent the occurrence of failure by a battery short circuit by a pinhole. Gas permeability is secured, safety of a battery is improved, and the loss of balance of internal pressure between a positive electrode and a negative electrode is prevented.

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CLAIMS

[Claim(s)]
[Claim 1] The separator for alkaline cells which is a separator for alkaline cells which consists of a nonwoven fabric with which it comes to mix ** sulfonation fiber and a polyolefin fiber, said nonwoven fabric is sulfonated, and becomes, and is characterized by said ** sulfonation fiber being a continuous fiber.
[Claim 2] The separator for alkaline cells according to claim 1 with which the diameter of fiber of said ** sulfonation fiber is characterized by being 0.3-10 micrometers.
[Claim 3] The separator for alkaline cells according to claim 1 or 2 characterized by said ** sulfonation fiber consisting of one or more fiber chosen from the group of polystyrene system fiber, polyvinyl naphthalene system fiber, polyether sulphone system fiber, or polycarbonate system fiber.
[Claim 4] The separator for alkaline cells according to claim 1 or 2 characterized by said ** sulfonation fiber consisting of syndiotactic system polystyrene.
[Claim 5] The separator for alkaline cells according to claim 1 to 4 with which said at least 20% of the weight of polyolefin fiber is characterized by the diameter of fiber being heat welding nature fiber 8 micrometers or more.
[Claim 6] The separator for alkaline cells according to claim 5 with which said diameter of fiber is characterized by heat welding fiber 8 micrometers or more being a bicomponent fiber of polypropylene and polyethylene.
[Claim 7] The separator for alkaline cells according to claim 1 to 6 with which the ** sulfonation fiber in said nonwoven fabric is characterized by coming to be sulfonated alternatively.
[Claim 8] the nonwoven fabric which blew the olefin system staple fiber into this extrusion object, and was mixed and united with homogeneity while extruding olefin system resin melt and ** sulfonation resin melt from the adjoining orifice and carrying out the melt blow -- SO3 with a temperature of 10-40 degrees C of 0.01 - 15% volume % The manufacture approach of the separator for alkaline cells characterized by carrying out sulfonation processing by gas.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the separator for alkali rechargeable batteries.
[0002]
[Description of the Prior Art] Conventionally, while preventing the short circuit of the positive electrode and negative electrode of an alkaline cell, the electrolytic solution was held, and the separator has been used in order to advance a charge-and-discharge reaction smoothly. Aiming at the further high-capacity-izing of a cell, thin shape-ization of a separator has been required especially in recent years. In the thin separator, the reinforcement which the nonwoven fabric with little eyes unevenness is called for in order to avoid strengthening electrolytic-solution holdout more and generating of a pinhole, in addition is not conventionally inferior to elegance, and high gas permeability are needed.
[0003] As a separator coping with the above-mentioned technical problems, such as electrolytic-solution solution retention, compatibility with the electrolytic solution is high and the separator which introduced the stable sulfonic group into coincidence thermally is already known.
[0004] For example, the separator which introduced the sulfonic group into the organism of a polyolefine system is indicated by JP,58-175256,A. However, this separator was an elevated temperature of 100-120 degrees C in concentrated sulfuric acid, and since long duration processing was carried out and it was obtained, and it was the separator of 25 minutes - 1 hour with which sulfonation advanced to the interior of fiber, and the fall of fiber itself on the strength was caused and the desorption phenomenon on the front face of fiber arose, it had the problem that the amount of sulfonic groups on the front face of fiber did not go up. It was a problem especially with the serious fall on the strength by hydrophilization processing in the case of a thin separator.
[0005] As the above-mentioned solution means, the separator which processed the polyolefine system nonwoven fabric with fluorine gas and a sulfur dioxide is indicated by JP,10-7829,A. However, since this separator had essentially given a lot of hydrophilic radicals to the polyolefine material with low chemical reactivity, the fall on the strength was remarkable, and the handling of fluorine gas including waste gas processing was complicated, and was what has a problem also industrially.
[0006] The inclination for the effectiveness of sulfonation to become low since the exposure to the fiber front face of the reinforcement of the fiber behind spinning not only becoming inadequate since, as for this separator, fiber consists of mixing [not a polyolefine single component but] resin, although the separator which made fiber after mixing polyolefin resin and polystyrene resin on resin level to JP,4-174964,A as an another solution means, and was sulfonated with concentrated sulfuric acid at low temperature is indicated but polystyrene resin is not enough was suited.
[0007] Although polystyrene was mixed in division fiber and the sulfonated separator was indicated by JP,8-273654,A, since it was used for polyethylene where polystyrene resin is mixed beforehand, like above-mentioned JP,4-174964,A, polystyrene tended to be buried and the effectiveness of sulfonation was inadequate, and since sulfonation processing was carried out by the oleum, it was not the separator which was compatible in reinforcement and high electrolytic-solution holdout like above-mentioned JP,58-175256,A. Furthermore, in order to use the fiber which cut fiber length to 10mm or less since the wet paper-making method was used for this separator, nonwoven fabric reinforcement was essentially inadequate.
[0008] Moreover, it was difficult to miss the reactant gas in which permeability carries out a byproduction to it low in the nonwoven fabric created at 100% of melt blow super-thin fiber although the separator which reinforcement carried out the laminating of the high nonwoven fabric, and unified although it was homogeneous and the melt blowing method nonwoven fabric with a high fiber consistency and the homogeneity by the dry type card method were low is

indicated by JP,5-182654,A, and reinforcement's was inadequate.
[0009] Electrolytic-solution solution retention is good, the homogeneity of a nonwoven fabric is high, and the present condition is that the separator of high intensity and quantity gas permeability is not obtained as explained above.
[0010]
[Problem(s) to be Solved by the Invention] This invention is made in view of the above-mentioned present condition, and aims at offering the separator for alkaline cells which can attain the property of four points as follows to coincidence on high level.
1. Secure high electrolytic-solution holdout and aim at improvement in a life of a cell.
2. By high intensity-ization, the activity interruption by the improvement in workability at the time of a cell assembly, i.e., cutting etc., can be avoided.
3. The homogeneity of a separator is improved (eyes unevenness is reduced) and defect generating by the cell short circuit by the pinhole can be avoided.
4. Secure the gas permeability more than fixed needed, aim at improvement in safety of a cell, prevent forward and balance collapse of the internal pressure of a negative electrode to coincidence, and aim at improvement in a battery life.
[0011] this invention persons found out that a good separator was obtained by using the continuous fiber for raising electrolytic-solution holdout, homogeneity, and gas permeability as ** sulfonation fiber using the thick fiber for raising the function of maintenance on the strength as a polyolefin fiber, as a result of inquiring paying attention to the functional assignment of a polyolefin fiber and the ** sulfonation fiber represented by polystyrene, in order to obtain the above-mentioned separator for alkaline cells.
[0012] Furthermore, apart from the above-mentioned thick fiber as olefin, it found out that homogeneity and gas permeability became more good by adding the super-thin fiber of continuation, using super-thin fiber as ** sulfonation fiber.
[0013] Furthermore, when sulfonating the above-mentioned nonwoven fabric, it found out that reinforcement might be raised further by sulfonating the front face of ** sulfonation fiber alternatively.
[0014] in addition, ** -- the separator [like] extruded olefin system fiber and ** sulfonation fiber by turns from the orifice which adjoins by the melt blowing method, and found out that it could produce by blowing the staple fiber of a thick olefin system into coincidence.
[0015] This invention is completed as a result of inquiring further in piles in the above-mentioned knowledge.
[0016]
[Means for Solving the Problem] That is, this invention offers the separator for alkaline cells which is a separator for alkaline cells which consists of a nonwoven fabric with which it comes to mix ** sulfonation fiber and a polyolefin fiber, said nonwoven fabric is sulfonated, and becomes, and is characterized by said ** sulfonation fiber being a continuous fiber.
[0017] The diameter of fiber of said ** sulfonation fiber of the desirable embodiment of the separator for alkaline cells of this invention is 0.3-10 micrometers.
[0018] The desirable embodiment of the separator for alkaline cells of this invention consists of one or more fiber as which said ** sulfonation fiber is chosen from the group of polystyrene system fiber, polyvinyl naphthalene system fiber, polyether sulphone system fiber, or polycarbonate system fiber.
[0019] As for the desirable embodiment of the separator for alkaline cells of this invention, said ** sulfonation fiber consists of syndiotactic system polystyrene.
[0020] Said at least 20% of the weight of polyolefin fiber is [the diameter of fiber of the desirable embodiment of the separator for alkaline cells of this invention] heat welding nature fiber 8 micrometers or more.
[0021] Said diameter of fiber is [the heat welding fiber 8 micrometers or more of the desirable embodiment of the separator for alkaline cells of this invention] a bicomponent fiber of polypropylene and polyethylene.
[0022] As for the desirable embodiment of the separator for alkaline cells of this invention, it comes to sulfonate the ** sulfonation fiber in said nonwoven fabric alternatively.
[0023] Moreover, this invention is SO3 with a temperature of 10-40 degrees C of 0.01 - 15% volume % about the nonwoven fabric which blew the olefin system staple fiber into this extrusion object, and was mixed and united with homogeneity while extruding olefin system resin melt and ** sulfonation resin melt from the adjoining orifice and carrying out the melt blow. The manufacture approach of the separator for alkaline cells which carries out sulfonation processing by gas is offered.
[0024]
[Embodiment of the Invention] Especially if the ** sulfonation fiber used for this invention is fiber which used as the

raw material the ingredient which is easy to sulfonate from a polyolefin fiber, it is not limited, and it says the polymer which has in intramolecular the ring represented by the benzene ring. Furthermore, specifically, polystyrene polystyrene system polymers, such as polystyrene, poly methyl styrene, and poly ethyl styrene, a polyvinyl naphthalene system polymer, a polyether sulphone system polymer, a polycarbonate system polymer, etc. are mentioned. Especially, polystyrene is the most desirable, and especially since especially syndiotactic system polystyrene is good in respect of thermal resistance and reinforcement, it is desirable.

[0025] Its 0.3-10 micrometers are desirable, and if the diameter of fiber of the ** sulfonation fiber used for this invention is 1-8 micrometers, it is more desirable. ** sulfonation fiber is because it is desirable that it is a key objective to raise the rate of sulfonation, and it is super-thin fiber with relative high surface area. Moreover, making it super-thin to coincidence raises homogeneity, and it leads to reducing the possibility of pinhole generating. When the diameter of fiber exceeds 10 micrometers, a touch area with sulfonation drugs decreases, reservation of the high rate of sulfonation becomes difficult, when the diameter of fiber is less than 0.3 micrometers, even if it carries out amelioration by the below-mentioned polyolefin fiber, the fiber interspace spare time of a separator is shortened and required reservation of gas permeability becomes difficult in the separator for alkali rechargeable batteries.

[0026] The ** sulfonation fiber used for this invention needs to be a continuous fiber. Although it is a key objective to raise the rate of sulfonation, when reinforcement is extremely weak, even if ** sulfonation fiber carries out amelioration by the below-mentioned polyolefin fiber, it becomes difficult [it / to secure separator reinforcement]. Since ** sulfonation fiber is not dissolved, it is difficult fiber to heat ** sulfonation super-thin fiber and to carry out on-the-strength maintenance by welding at below the melting point of the polyolefin fiber to interweave. In addition, the above-mentioned continuous fiber is fiber which extruded the raw material polymer continuously and was obtained with spinning, and the fiber whose fiber length is at least 20cm or more is said. Furthermore, although it said above that ** sulfonation fiber is difficult welding, it becomes possible to perform welding on an intersection by carrying out the confounding of the fiber before [to solidify] melt spinning was carried out from the spinning nozzle.

[0027] The manufacture approach of the ** sulfonation fiber used for this invention has the desirable melt blowing method. After specifically extruding the raw material resin of the fused ** sulfonation fiber by pressurization gas and adding extension by suction, it is the approach of nonwoven-fabric-izing at the same time it solidifies on networks, such as a metal.

[0028] The polyolefin fiber used for this invention has polyethylene and desirable polypropylene. It is because alkali resistance is good.

[0029] It is desirable that at least 20% of the weight of the polyolefin fiber used for this invention is [a fiber system] heat welding nature fiber 8 micrometers or more, and it is more desirable if it is 8-30 micrometers. Although it becomes possible to raise homogeneity and to reduce the possibility of pinhole generating on extremely low level when ** sulfonation fiber is written as super-thin fiber and this polyolefin fiber is made into the whole quantity and super-thin fiber, it becomes difficult to secure the gas permeability more than fixed needed.

[0030] Moreover, the above-mentioned polyolefin fiber is desirable if it is a diameter of fiber of 1.2 times or more of ** sulfonation super-thin fiber at least, and if it is a diameter of fiber of 1.5 times or more, it is more desirable. It is because it is required when securing gas permeability.

[0031] If the further above-mentioned polyolefin fiber is a PP/PE bicomponent fiber (the heart / sheath type, or side-by-side mold), it is desirable. It is for aiming at improvement in on the strength of a nonwoven fabric. It becomes possible to improve reinforcement by carrying out welding of the PE part. Furthermore, ultrahigh-molecular-weight PE fiber also employs the very high reinforcement efficiently, and it becomes it is effectively usable and possible to raise reinforcement of it by carrying out welding partially.

[0032] Furthermore, it is an important point to mix the above-mentioned ** sulfonation super-thin fiber and a polyolefin fiber with the thick diameter of fiber to homogeneity from a viewpoint which raises homogeneity. the above which carried out spinning beforehand by the approach called KOFOMU in the case of melt blow spinning -- the approach of blowing a thick polyolefin fiber and unifying is the most desirable at the point which raises homogeneity. As a gestalt of the fiber in this case, it is a staple fiber with a fiber length of 2-8cm that it is a staple fiber with a fiber length of 1-10cm desirable still more desirably. Since the reinforcement effectiveness becomes inadequate and it becomes difficult to blow fiber into homogeneity desirably in being longer than 10cm in being shorter than 1cm, fiber length is not desirable. Moreover, it is also desirable to attach crimp to the above-mentioned staple fiber in respect of the improvement in on the strength of a nonwoven fabric.

[0033] Furthermore, it is also effective in a polyolefin fiber to mix polyolefine system super-thin fiber. When carrying out spinning of the ** sulfonation super-thin fiber, and two sorts of thermoplastics uses the compound nozzle in which spinning is possible and carries out spinning of the polyolefine system super-thin fiber to ** sulfonation super-thin

fiber and coincidence, while a confounding and welding happen to two sorts of super-thin fiber effectively and it is useful to improvement in maintenance on the strength by the melt blowing method especially, it is useful to the homogeneous improvement in a nonwoven fabric. However, in order to avoid the fall of air permeability as above-mentioned, it is 0 - 60% of range to mix polyolefine system super-thin fiber in 0 - 80% of range of all polyolefin fibers desirable especially desirably. It is necessary to suppose that the mixed rate of polyolefine system super-thin fiber is reduced, and polyolefine system super-thin fiber is not mixed depending on the case (0% of mixing percentage) highly [the rate of the amount of ** sulfonation super-thin fiber], so that it may become necessary minimum air permeability when the diameter of fiber is low. Indispensable air permeability is a value 9 cc/cm2 and more than s.

[0034] The range of the mixed ratio (weight ratio) of a polyolefin fiber and ** sulfonation fiber being in the range of 1:4-4:1 is 1:3-3:1 desirable still more desirably. If there are extremely few one of fiber rates, since it becomes difficult to maintain the balance of a functional assignment which is the description of this invention, it is not desirable.

[0035] Separator manufacture of this invention is attained by carrying out sulfonation processing on conditions milder than the case where the nonwoven fabric which used the conventional polyolefine system as the principal component for the nonwoven fabric with the description shown above is sulfonated.

[0036] If mild sulfonation conditions are sulfonation processings by the sulfuric acid, processing of 90 degrees C or less is processing at low temperature 70 degrees C or less desirable still more desirably. There is no sulfonated surface desorption and such ** sulfonation super-thin fiber used by this invention also in low temperature treatment can attain the very high amount of sulfonic groups easily. Furthermore, in such mild sulfonation conditions, since sulfonation of a polyolefin fiber is slight, problems which elegance has conventionally, such as a fall of the reinforcement of a polyolefin fiber and sulfonated desorption of a part, are not produced.

[0037] Furthermore, SO3 The sulfonation processing by gas is also effective. The range of 10-40 degrees C is desirable still more desirable, and the range of processing temperature is 15-30 degrees C. SO3 Although the approach of gas of using gamma mold sulfuric anhydride, carrying out nitrogen dilution is the simplest, since the congealing point is 16 degrees C, even if gamma mold sulfuric anhydride carries out dilution in nitrogen gas etc. at temperature lower than 10 degrees C, it is difficult to gasify in the condition with stable concentration, and it is not desirable. Moreover, in the case of 40 degrees C or more, since reactivity increases too much and the fall of a polyolefin fiber on the strength becomes large, it is not desirable. moreover, SO3 occupied in [all] gas a control item also with the important concentration of gas -- it is -- SO3 gas concentration is in the range of 0.01 - 15 volume % -- ****** -- it is the range of 0.05 - 10 volume % still more desirably. When concentration exceeds 10 volume %, since the fall of a polyolefin fiber on the strength becomes large, it is not desirable. Although manufacture of a separator is possible if reaction time is lengthened since the reactivity of ** sulfonation fiber is very high when concentration is less than 0.01 volume %, it is not desirable from Men of a manufacturing cost.

[0038] the above -- it is 85% or more to carry out using the separator with the diameter of fiber equivalent to the object used with the separator of this invention as a diagnosis of mild sulfonation conditions created at 100% of polyolefin fibers on the conditions to which the reinforcement carries out 75% or more of maintenance on the strength after sulfonation on the basis of sulfonation before desirable still more desirably. The above-mentioned value is defined as polyolefine retention (%) on the strength, and is further explained to a detail in the below-mentioned example. In such conditions, although ** sulfonation super-thin fiber is fully sulfonated, sulfonation of a polyolefin fiber is a minute amount and sufficient maintenance on the strength of it is attained. On the contrary, when polyolefine retention on the strength creates a separator on the strong sulfonation conditions which correspond to less than 75%, since the original purpose which sulfonation of a polyolefin fiber progresses too much and mainly holds reinforcement cannot be attained, it is not desirable.

[0039] Moreover, although the oleum heated at 100 degrees C or more in manufacture of the conventional polyolefine system sulfonic group content separator has been used, since reactivity is too high in this invention, use is difficult. However, it is usable, if temperature management is carried out and special management of a halt etc. is especially reacted to 10-40-degree C low temperature by introducing a washing process into coincidence promptly after processing within in several seconds.

[0040] Whenever [sulfonation-with whole nonwoven fabric] serves as a solution retention standard of a separator. For this reason, it is desirable still more desirable to control the processing time etc. to become the range of 0.5 - 20 element %, and the sulfur content of the surface layer which is the index of whenever [sulfonation] is the range of 2 - 15 element %. When the sulfur content of a fiber surface layer is lower than 0.5 element %, the holdout of the electrolytic solution is not enough and desirable. When sulfur content is higher than 20 element %, reaction time is too long, and since it is presumed that superfluous sulfonation is progressing and exfoliation and an extreme fall on the strength of a surface layer take place, it is not desirable.

[0041] This invention is usable the most effective in a thin separator with a thickness of 70-140 micrometers. Since solution retention runs short with a separator with a thickness of 70 micrometers or less, it is not desirable. Moreover, in the cell in the application of "a medical-application way, an emergency power supply, an electric vehicle", etc. with which advanced dependability is demanded from it being the synthetically excellent separator which holds the gas permeability more than fixed with high electrolytic-solution holdout, sufficient high intensity, and sufficient homogeneity, and moreover holds a heat-resistant high sulfonic group, thickness of this invention is effectively usable also in the separator of the range which is 140-220 micrometers.

[0042]

[Example] The example of this invention is used for below and it explains to it concretely. In addition, the physical properties shown in the example were measured by the following approaches.

[0043] b. It measured by the X-ray photoelectron spectroscopy currently called for short a sulfur content ESCA or XPC. Measurement used the Shimadzu ESCA750 mold and, specifically, analysis used the ESCAPAC760 mold. The content element containing carbon was measured and was displayed by element % of the sulfur contained.

[0044] b. Air permeability JIS L Measured value in the Flagyl mold testing machine according to permeability A law given in 1096 was made into the air permeability in this invention.

[0045] c. The thickness of the thickness separator of a separator was measured under the load of 300kPa. Specifically, 10 Ns of measuring force and a measuring plane measured using the micrometer (1102 to MitutoyoM25 mold) which is 6mmphi.

[0046] d. A sample with a width of face [of 5cm] and a die length of 15cm is used for the reinforcement of the separator of a separator on the strength, and it is JISL. According to 1068 (the tensile test approach of textiles), the tension rate was used as a part for 30cm/, having used grip spacing as 10cm, and the tensile strength in the direction of length (MD) was measured using the tensilon RTM-100 mold testing machine.

[0047] Example 1 polypropylene and SHINJI nerd theque polystyrene were extruded at the temperature of 295 degrees C by turns from the adjoining orifice. Solitary-foramen discharge quantity was taken as polypropylene =0.3g/min., and SHINJI nerd theque polystyrene =0.5g/min. 0.8 morekg/cm2 It was made to ******-ize by 300-degree C airstream, the bicomponent fiber (Chisso Corp., ES fiber, the diameter of fiber of 16 micrometers, die length of 50mm) of polypropylene/polyethylene was blown into coincidence, and three sorts of fiber created the nonwoven fabric by which homogeneity mixing was carried out. The heat press was carried out at 100 degrees C, and it considered as the thickness of 120 micrometers. The schematic diagram of a nonwoven fabric listing device was shown in drawing 1 . The above-mentioned sample is started in size with a width-of-face [of 10cm] x die length of 60cm, and it is SO3. With the nitrogen gas 10 volume % Containing gas, it carried out by processing for 30 seconds at the room temperature (25 degrees C). After processing permuted the reaction vessel with a lot of nitrogen gas, and suspended the sulfonation reaction. Used SO3 The Nisso ape fan by Nippon Soda Co., Ltd. was used for gas by evaporating with nitrogen gas. The used processor was shown in drawing 2 .

[0048] Using the created separator, nickel / hydrogen rechargeable battery of capacity 2500mAh were created, charge and discharge were repeated in 0.4C, and the discharge capacity maintenance factor was measured. Discharge capacity made 100% discharge capacity in the initial cycle after finishing 1 - 2 times of the preliminary charges and discharges for activation of a hydrogen storing metal alloy, and measured the maintenance factor of the discharge capacity when repeating a charge-and-discharge cycle. The potassium-hydroxide water solution was used for the electrolytic solution. The number of cycles when a discharge capacity maintenance factor falling to 50% was evaluated as a life of a cell.

[0049] The result of the life evaluation by the creation conditions, physical properties, and discharge capacity maintenance factor of a separator was summarized in Table 1.

[0050] Furthermore, for the check of the strength of sulfonation conditions, without using SHINJI nerd theque polystyrene, in the above-mentioned example 1, the nonwoven fabric with the equivalent diameter of fiber was created, and the tensile strength was measured only by the polyolefin fiber (T0). Furthermore, after carrying out sulfonation processing on the same sulfonation conditions as an example 1, the tensile strength was measured (T1). Here, the value calculated by (T1/T0) *100(%) was defined as polyolefine retention (%) on the strength, and was made into the scale of measurement of sulfonation conditions on the strength. The polyolefine retention on the strength in a result and an example 1 was 95% and a high value, its rate of sulfonation of a polyolefin fiber was small, and it was checked that polystyrene system super-thin fiber is sulfonated alternatively. Hereafter, in each example, the polyolefine retention on the strength in each example is measured with the nonwoven fabric using the corresponding polyolefin fiber.

[0051] The mixed ratio, the diameter of fiber, and SO3 of the fiber used example 2-3 Except having changed the sulfonation time amount by gas, it is the approach of the same approach as an example 1, and separator creation and evaluation were carried out. The result of the life evaluation by the creation conditions, physical properties, and

discharge capacity maintenance factor of a separator was summarized in Table 1.

[0052] Except having processed an example 4 - 5 sulfonation processing with the sulfuric acid, it is the same law as examples 1-2, and separator creation and evaluation were carried out. The result of the life evaluation by the creation conditions, physical properties, and discharge capacity maintenance factor of a separator was summarized in Table 1.

[0053] About the polyolefine 100% nonwoven fabric which does not contain example of comparison 1 ** sulfonation fiber, it is SO3. It processed at 110 degrees C by the oleum contained 15% of the weight, and the same measurement as an example 1 was carried out. They were a surface layer sulfur content and a value with strong insufficient both sides. The result was summarized in Table 2.

[0054] The polyolefine 100% nonwoven fabric which does not contain example of comparison 2 ** sulfonation fiber was processed on the same mild sulfonation conditions as an example 1. Although only the surface layer was sulfonated, the surface layer sulfur content was a low value, and solution retention of the result was not enough, and it was inadequate. [of the function as a separator] The result was summarized in Table 2.

[0055] Although spinning was carried out by the same melt blowing method as an example 1 using example of comparison 3 polypropylene, and SHINJI nerd theque polystyrene Although the entrainment of a bicomponent fiber evaluated by performing sulfonation processing for this nonwoven fabric that obtained the nonwoven fabric with a thickness of 120 micrometers with a 120-degree C heat press on the same sulfonation conditions as an example 1, and creating a separator after creating the nonwoven fabric, without carrying out Since air permeability was low, the balance of internal pressure collapsed in the charge-and-discharge cycle, and the extreme fall of a life occurred. The result was summarized in Table 2.

[0056]

[Table 1]

	実施例1	実施例2	実施例3	実施例4	実施例5
表面層硫黄含有量（元素%）	6．0	3．8	10．9	4．2	3．5
不織布組成 （含有率　重量%） ［繊維径　μm］	sPs(50)[7] PP(30)[5] PPE(20)[16]	sPs(35)[7] PP(30)[5] PPE(35)[16]	sPs(65)[2] PP(15)[5] PPE(20)[12]	sPs(50)[7] PP(30)[5] PPE(20)[16]	sPs(50)[10] PP(30)[8] PPE(20)[12]
スルホン化条件 （温度） （時間）	SO3ガス 25℃ 30秒	SO3ガス 25℃ 25秒	SO3ガス 25℃ 40秒	硫酸 60℃ 25分	硫酸 60℃ 16分
引っ張り強度（kgf／5cm幅）	10．0	10．8	11．9	9．4	8．0
目付（g／m²）	49	52	65	63	48
透気度（cc/cm2・s）	15．9	20．6	10．0	16．8	16．2
厚み（μm）	120	130	105	120	105
サイクル寿命（サイクル）	580	545	590	505	485
ポリオレフィン強度保持率(%)	95	95	92	86	89

sPs＝シンジオタクティクポリスチレン
PP＝ポリプロピレン
PPE＝ポリプロピレン／ポリエチレン（芯／鞘繊維）

[0057]

[Table 2]

	比較例1	比較例2	比較例3
表面層硫黄含有量（元素%）	2．2	0．97	1．9
不織布組成 （含有率　重量%） ［繊維径　μm］	PP(50)［5］ PPE(50)[10]	PP(50)［5］ PPE(50)[10]	PP+sPs(85)[11] PPE(15)[16]
スルホン化条件 （温度） （時間）	発煙硫酸 110℃ 25分	SO3ガス 25℃ 30秒	SO3ガス 25℃ 30秒
引っ張り強度（kgf／5cm幅）	6．9	13．9	6．8
目付（g／m²）	45	52	48
透気度（cc/cm2・s）	16．8	15．3	29．8
厚み（μm）	120	130	130
サイクル寿命（ｻｲｸﾙ）	295	25	250
ポリオレフィン強度保持率(%)	70	96	97

sPs＝シンジオタクティクティクポリスチレン
PP＝ポリプロピレン
PPE＝ポリプロピレン／ポリエチレン（芯／鞘繊維）

[0058]
[Effect of the Invention] As mentioned above, this invention attains the property [required for the separator for alkaline cells] of four points as follows to coincidence on high level, and brings about the property which was excellent in the following to the cell which adopted this separator. 1: Secure high electrolytic-solution holdout and raise the life of a cell. 2: By high intensity-ization, it is ** without the activity interruption by the improvement in workability at the time of a cell assembly, i.e., cutting etc. 3: Improve the homogeneity of a separator (eyes unevenness is reduced) and abolish defect generating by the cell short circuit by the pinhole. 4: Secure the gas permeability more than fixed needed, and raise the cycle life of a cell at the same time it raises the safety of a cell. Moreover, above, since the description which has a sulfonic group stable thermal over a long period of time is in everything but four points, also in a severe service condition, prolonged charge and discharge are made possible. Furthermore, in thin separator creation, since it is effective, especially thickness contributes this invention to increase of cell capacity.

[Translation done.]

* NOTICES *

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the separator for alkali rechargeable batteries.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] Conventionally, while preventing the short circuit of the positive electrode and negative electrode of an alkaline cell, the electrolytic solution was held, and the separator has been used in order to advance a charge-and-discharge reaction smoothly. Aiming at the further high-capacity-izing of a cell, thin shape-ization of a separator has been required especially in recent years. In the thin separator, the reinforcement which the nonwoven fabric with little eyes unevenness is called for in order to avoid strengthening electrolytic-solution holdout more and generating of a pinhole, in addition is not conventionally inferior to elegance, and high gas permeability are needed.
[0003] As a separator coping with the above-mentioned technical problems, such as electrolytic-solution solution retention, compatibility with the electrolytic solution is high and the separator which introduced the stable sulfonic group into coincidence thermally is already known.
[0004] For example, the separator which introduced the sulfonic group into the organism of a polyolefine system is indicated by JP,58-175256,A. However, this separator was an elevated temperature of 100-120 degrees C in concentrated sulfuric acid, and since long duration processing was carried out and it was obtained, and it was the separator of 25 minutes - 1 hour with which sulfonation advanced to the interior of fiber, and the fall of fiber itself on the strength was caused and the desorption phenomenon on the front face of fiber arose, it had the problem that the amount of sulfonic groups on the front face of fiber did not go up. It was a problem especially with the serious fall on the strength by hydrophilization processing in the case of a thin separator.
[0005] As the above-mentioned solution means, the separator which processed the polyolefine system nonwoven fabric with fluorine gas and a sulfur dioxide is indicated by JP,10-7829,A. However, since this separator had essentially given a lot of hydrophilic radicals to the polyolefine material with low chemical reactivity, the fall on the strength was remarkable, and the handling of fluorine gas including waste gas processing was complicated, and was what has a problem also industrially.
[0006] The inclination for the effectiveness of sulfonation to become low since the exposure to the fiber front face of the reinforcement of the fiber behind spinning not only becoming inadequate since, as for this separator, fiber consists of mixing [not a polyolefine single component but] resin, although the separator which made fiber after mixing polyolefin resin and polystyrene resin on resin level to JP,4-174964,A as an another solution means, and was sulfonated with concentrated sulfuric acid at low temperature is indicated but polystyrene resin is not enough was suited.
[0007] Although polystyrene was mixed in division fiber and the sulfonated separator was indicated by JP,8-273654,A, since it was used for polyethylene where polystyrene resin is mixed beforehand, like above-mentioned JP,4-174964,A, polystyrene tended to be buried and the effectiveness of sulfonation was inadequate, and since sulfonation processing was carried out by the oleum, it was not the separator which was compatible in reinforcement and high electrolytic-solution holdout like above-mentioned JP,58-175256,A. Furthermore, in order to use the fiber which cut fiber length to 10mm or less since the wet paper-making method was used for this separator, nonwoven fabric reinforcement was essentially inadequate.
[0008] Moreover, it was difficult to miss the reactant gas in which permeability carries out a byproduction to it low in the nonwoven fabric created at 100% of melt blow super-thin fiber although the separator which reinforcement carried out the laminating of the high nonwoven fabric, and unified although it was homogeneous and the melt blowing method nonwoven fabric with a high fiber consistency and the homogeneity by the dry type card method were low is indicated by JP,5-182654,A, and reinforcement's was inadequate.
[0009] Electrolytic-solution solution retention is good, the homogeneity of a nonwoven fabric is high, and the present condition is that the separator of high intensity and quantity gas permeability is not obtained as explained above.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, this invention attains the property [required for the separator for alkaline cells] of four points as follows to coincidence on high level, and brings about the property which was excellent in the following to the cell which adopted this separator. 1: Secure high electrolytic-solution holdout and raise the life of a cell. 2: By high intensity-ization, it is ** without the activity interruption by the improvement in workability at the time of a cell assembly, i.e., cutting etc. 3: Improve the homogeneity of a separator (eyes unevenness is reduced) and abolish defect generating by the cell short circuit by the pinhole. 4: Secure the gas permeability more than fixed needed, and raise the cycle life of a cell at the same time it raises the safety of a cell. Moreover, above, since the description which has a sulfonic group stable thermal over a long period of time is in everything but four points, also in a severe service condition, prolonged charge and discharge are made possible. Furthermore, in thin separator creation, since it is effective, especially thickness contributes this invention to increase of cell capacity.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention is made in view of the above-mentioned present condition, and aims at offering the separator for alkaline cells which can attain the property of four points as follows to coincidence on high level.
1. Secure high electrolytic-solution holdout and aim at improvement in a life of a cell.
2. By high intensity-ization, the activity interruption by the improvement in workability at the time of a cell assembly, i.e., cutting etc., can be avoided.
3. The homogeneity of a separator is improved (eyes unevenness is reduced) and defect generating by the cell short circuit by the pinhole can be avoided.
4. Secure the gas permeability more than fixed needed, aim at improvement in safety of a cell, prevent forward and balance collapse of the internal pressure of a negative electrode to coincidence, and aim at improvement in a battery life.
[0011] this invention persons found out that a good separator was obtained by using the continuous fiber for raising electrolytic-solution holdout, homogeneity, and gas permeability as ** sulfonation fiber using the thick fiber for raising the function of maintenance on the strength as a polyolefin fiber, as a result of inquiring paying attention to the functional assignment of a polyolefin fiber and the ** sulfonation fiber represented by polystyrene, in order to obtain the above-mentioned separator for alkaline cells.
[0012] Furthermore, apart from the above-mentioned thick fiber as olefin, it found out that homogeneity and gas permeability became more good by adding the super-thin fiber of continuation, using super-thin fiber as ** sulfonation fiber.
[0013] Furthermore, when sulfonating the above-mentioned nonwoven fabric, it found out that reinforcement might be raised further by sulfonating the front face of ** sulfonation fiber alternatively.
[0014] in addition, ** -- the separator [like] extruded olefin system fiber and ** sulfonation fiber by turns from the orifice which adjoins by the melt blowing method, and found out that it could produce by blowing the staple fiber of a thick olefin system into coincidence.
[0015] This invention is completed as a result of inquiring further in piles in the above-mentioned knowledge.

[Translation done.]

MEANS

[Means for Solving the Problem] That is, this invention offers the separator for alkaline cells which is a separator for alkaline cells which consists of a nonwoven fabric with which it comes to mix ** sulfonation fiber and a polyolefin fiber, said nonwoven fabric is sulfonated, and becomes, and is characterized by said ** sulfonation fiber being a continuous fiber.
[0017] The diameter of fiber of said ** sulfonation fiber of the desirable embodiment of the separator for alkaline cells of this invention is 0.3-10 micrometers.
[0018] The desirable embodiment of the separator for alkaline cells of this invention consists of one or more fiber as which said ** sulfonation fiber is chosen from the group of polystyrene system fiber, polyvinyl naphthalene system fiber, polyether sulphone system fiber, or polycarbonate system fiber.
[0019] As for the desirable embodiment of the separator for alkaline cells of this invention, said ** sulfonation fiber consists of syndiotactic system polystyrene.
[0020] Said at least 20% of the weight of polyolefin fiber is [the diameter of fiber of the desirable embodiment of the separator for alkaline cells of this invention] heat welding nature fiber 8 micrometers or more.
[0021] Said diameter of fiber is [the heat welding fiber 8 micrometers or more of the desirable embodiment of the separator for alkaline cells of this invention] a bicomponent fiber of polypropylene and polyethylene.
[0022] As for the desirable embodiment of the separator for alkaline cells of this invention, it comes to sulfonate the ** sulfonation fiber in said nonwoven fabric alternatively.
[0023] Moreover, this invention is SO3 with a temperature of 10-40 degrees C of 0.01 - 15% volume % about the nonwoven fabric which blew the olefin system staple fiber into this extrusion object, and was mixed and united with homogeneity while extruding olefin system resin melt and ** sulfonation resin melt from the adjoining orifice and carrying out the melt blow. The manufacture approach of the separator for alkaline cells which carries out sulfonation processing by gas is offered.
[0024]
[Embodiment of the Invention] Especially if the ** sulfonation fiber used for this invention is fiber which used as the raw material the ingredient which is easy to sulfonate from a polyolefin fiber, it is not limited, and it says the polymer which has in intramolecular the ring represented by the benzene ring. Furthermore, specifically, polystyrene polystyrene system polymers, such as polystyrene, poly methyl styrene, and poly ethyl styrene, a polyvinyl naphthalene system polymer, a polyether sulphone system polymer, a polycarbonate system polymer, etc. are mentioned. Especially, polystyrene is the most desirable, and especially since especially syndiotactic system polystyrene is good in respect of thermal resistance and reinforcement, it is desirable.
[0025] Its 0.3-10 micrometers are desirable, and if the diameter of fiber of the ** sulfonation fiber used for this invention is 1-8 micrometers, it is more desirable. ** sulfonation fiber is because it is desirable that it is a key objective to raise the rate of sulfonation, and it is super-thin fiber with relative high surface area. Moreover, making it super-thin to coincidence raises homogeneity, and it leads to reducing the possibility of pinhole generating. When the diameter of fiber exceeds 10 micrometers, a touch area with sulfonation drugs decreases, reservation of the high rate of sulfonation becomes difficult, when the diameter of fiber is less than 0.3 micrometers, even if it carries out amelioration by the below-mentioned polyolefin fiber, the fiber interspace spare time of a separator is shortened and required reservation of gas permeability becomes difficult in the separator for alkali rechargeable batteries.
[0026] The ** sulfonation fiber used for this invention needs to be a continuous fiber. Although it is a key objective to raise the rate of sulfonation, when reinforcement is extremely weak, even if ** sulfonation fiber carries out amelioration by the below-mentioned polyolefin fiber, it becomes difficult [it / to secure separator reinforcement]. Since ** sulfonation fiber is not dissolved, it is difficult fiber to heat ** sulfonation super-thin fiber and to carry out on-

the-strength maintenance by welding at below the melting point of the polyolefin fiber to interweave. In addition, the above-mentioned continuous fiber is fiber which extruded the raw material polymer continuously and was obtained with spinning, and the fiber whose fiber length is at least 20cm or more is said. Furthermore, although it said above that ** sulfonation fiber is difficult welding, it becomes possible to perform welding on an intersection by carrying out the confounding of the fiber before [to solidify] melt spinning was carried out from the spinning nozzle.

[0027] The manufacture approach of the ** sulfonation fiber used for this invention has the desirable melt blowing method. After specifically extruding the raw material resin of the fused ** sulfonation fiber by pressurization gas and adding extension by suction, it is the approach of nonwoven-fabric-izing at the same time it solidifies on networks, such as a metal.

[0028] The polyolefin fiber used for this invention has polyethylene and desirable polypropylene. It is because alkali resistance is good.

[0029] It is desirable that at least 20% of the weight of the polyolefin fiber used for this invention is [a fiber system] heat welding nature fiber 8 micrometers or more, and it is more desirable if it is 8-30 micrometers. Although it becomes possible to raise homogeneity and to reduce the possibility of pinhole generating on extremely low level when ** sulfonation fiber is written as super-thin fiber and this polyolefin fiber is made into the whole quantity and super-thin fiber, it becomes difficult to secure the gas permeability more than fixed needed.

[0030] Moreover, the above-mentioned polyolefin fiber is desirable if it is a diameter of fiber of 1.2 times or more of ** sulfonation super-thin fiber at least, and if it is a diameter of fiber of 1.5 times or more, it is more desirable. It is because it is required when securing gas permeability.

[0031] If the further above-mentioned polyolefin fiber is a PP/PE bicomponent fiber (the heart / sheath type, or side-by-side mold), it is desirable. It is for aiming at improvement in on the strength of a nonwoven fabric. It becomes possible to improve reinforcement by carrying out welding of the PE part. Furthermore, ultrahigh-molecular-weight PE fiber also employs the very high reinforcement efficiently, and it becomes it is effectively usable and possible to raise reinforcement of it by carrying out welding partially.

[0032] Furthermore, it is an important point to mix the above-mentioned ** sulfonation super-thin fiber and a polyolefin fiber with the thick diameter of fiber to homogeneity from a viewpoint which raises homogeneity. the above which carried out spinning beforehand by the approach called KOFOMU in the case of melt blow spinning -- the approach of blowing a thick polyolefin fiber and unifying is the most desirable at the point which raises homogeneity. As a gestalt of the fiber in this case, it is a staple fiber with a fiber length of 2-8cm that it is a staple fiber with a fiber length of 1-10cm desirable still more desirably. Since the reinforcement effectiveness becomes inadequate and it becomes difficult to blow fiber into homogeneity desirably in being longer than 10cm in being shorter than 1cm, fiber length is not desirable. Moreover, it is also desirable to attach crimp to the above-mentioned staple fiber in respect of the improvement in on the strength of a nonwoven fabric.

[0033] Furthermore, it is also effective in a polyolefin fiber to mix polyolefine system super-thin fiber. When carrying out spinning of the ** sulfonation super-thin fiber, and two sorts of thermoplastics uses the compound nozzle in which spinning is possible and carries out spinning of the polyolefine system super-thin fiber to ** sulfonation super-thin fiber and coincidence, while a confounding and welding happen to two sorts of super-thin fiber effectively and it is useful to improvement in maintenance on the strength by the melt blowing method especially, it is useful to the homogeneous improvement in a nonwoven fabric. However, in order to avoid the fall of air permeability as above-mentioned, it is 0 - 60% of range to mix polyolefine system super-thin fiber in 0 - 80% of range of all polyolefin fibers desirable especially desirably. It is necessary to suppose that the mixed rate of polyolefine system super-thin fiber is reduced, and polyolefine system super-thin fiber is not mixed depending on the case (0% of mixing percentage) highly [the rate of the amount of ** sulfonation super-thin fiber], so that it may become necessary minimum air permeability when the diameter of fiber is low. Indispensable air permeability is a value 9 cc/cm2 and more than s.

[0034] The range of the mixed ratio (weight ratio) of a polyolefin fiber and ** sulfonation fiber being in the range of 1:4-4:1 is 1:3-3:1 desirable still more desirably. If there are extremely few one of fiber rates, since it becomes difficult to maintain the balance of a functional assignment which is the description of this invention, it is not desirable.

[0035] Separator manufacture of this invention is attained by carrying out sulfonation processing on conditions milder than the case where the nonwoven fabric which used the conventional polyolefine system as the principal component for the nonwoven fabric with the description shown above is sulfonated.

[0036] If mild sulfonation conditions are sulfonation processings by the sulfuric acid, processing of 90 degrees C or less is processing at low temperature 70 degrees C or less desirable still more desirably. There is no sulfonated surface desorption and such ** sulfonation super-thin fiber used by this invention also in low temperature treatment can attain the very high amount of sulfonic groups easily. Furthermore, in such mild sulfonation conditions, since sulfonation of a

polyolefin fiber is slight, problems which elegance has conventionally, such as a fall of the reinforcement of a polyolefin fiber and sulfonated desorption of a part, are not produced.

[0037] Furthermore, SO3 The sulfonation processing by gas is also effective. The range of 10-40 degrees C is desirable still more desirable, and the range of processing temperature is 15-30 degrees C. SO3 Although the approach of gas of using gamma mold sulfuric anhydride, carrying out nitrogen dilution is the simplest, since the congealing point is 16 degrees C, even if gamma mold sulfuric anhydride carries out dilution in nitrogen gas etc. at temperature lower than 10 degrees C, it is difficult to gasify in the condition with stable concentration, and it is not desirable. Moreover, in the case of 40 degrees C or more, since reactivity increases too much and the fall of a polyolefin fiber on the strength becomes large, it is not desirable. moreover, SO3 occupied in [all] gas a control item also with the important concentration of gas -- it is -- SO3 gas concentration is in the range of 0.01 - 15 volume % -- ****** -- it is the range of 0.05 - 10 volume % still more desirably. When concentration exceeds 10 volume %, since the fall of a polyolefin fiber on the strength becomes large, it is not desirable. Although manufacture of a separator is possible if reaction time is lengthened since the reactivity of ** sulfonation fiber is very high when concentration is less than 0.01 volume %, it is not desirable from the field of a manufacturing cost.

[0038] the above -- it is 85% or more to carry out using the separator with the diameter of fiber equivalent to the object used with the separator of this invention as a diagnosis of mild sulfonation conditions created at 100% of polyolefin fibers on the conditions to which the reinforcement carries out 75% or more of maintenance on the strength after sulfonation on the basis of sulfonation before desirable still more desirably. The above-mentioned value is defined as polyolefine retention (%) on the strength, and is further explained to a detail in the below-mentioned example. In such conditions, although ** sulfonation super-thin fiber is fully sulfonated, sulfonation of a polyolefin fiber is a minute amount and sufficient maintenance on the strength of it is attained. On the contrary, when polyolefine retention on the strength creates a separator on the strong sulfonation conditions which correspond to less than 75%, since the original purpose which sulfonation of a polyolefin fiber progresses too much and mainly holds reinforcement cannot be attained, it is not desirable.

[0039] Moreover, although the oleum heated at 100 degrees C or more in manufacture of the conventional polyolefine system sulfonic group content separator has been used, since reactivity is too high in this invention, use is difficult. However, it is usable, if temperature management is carried out and special management of a halt etc. is especially reacted to 10-40-degree C low temperature by introducing a washing process into coincidence promptly after processing within in several seconds.

[0040] Whenever [sulfonation-with whole nonwoven fabric] serves as a solution retention standard of a separator. For this reason, it is desirable still more desirable to control the processing time etc. to become the range of 0.5 - 20 element %, and the sulfur content of the surface layer which is the index of whenever [sulfonation] is the range of 2 - 15 element %. When the sulfur content of a fiber surface layer is lower than 0.5 element %, the holdout of the electrolytic solution is not enough and desirable. When sulfur content is higher than 20 element %, reaction time is too long, and since it is presumed that superfluous sulfonation is progressing and exfoliation and an extreme fall on the strength of a surface layer take place, it is not desirable.

[0041] This invention is usable the most effective in a thin separator with a thickness of 70-140 micrometers. Since solution retention runs short with a separator with a thickness of 70 micrometers or less, it is not desirable. Moreover, in the cell in the application of "a medical-application way, an emergency power supply, an electric vehicle", etc. with which advanced dependability is demanded from it being the synthetically excellent separator which holds the gas permeability more than fixed with high electrolytic-solution holdout, sufficient high intensity, and sufficient homogeneity, and moreover holds a heat-resistant high sulfonic group, thickness of this invention is effectively usable also in the separator of the range which is 140-220 micrometers.

[Translation done.]

EXAMPLE

[Example] The example of this invention is used for below and it explains to it concretely. In addition, the physical properties shown in the example were measured by the following approaches.
[0043] b. It measured by the X-ray photoelectron spectroscopy currently called for short a sulfur content ESCA or XPC. Measurement used the Shimadzu ESCA750 mold and, specifically, analysis used the ESCAPAC760 mold. The content element containing carbon was measured and was displayed by element % of the sulfur contained.
[0044] b. Air permeability JIS L Measured value in the Flagyl mold testing machine according to permeability A law given in 1096 was made into the air permeability in this invention.
[0045] c. The thickness of the thickness separator of a separator was measured under the load of 300kPa. Specifically, 10 Ns of measuring force and a measuring plane measured using the micrometer (1102 to MitutoyoM25 mold) which is 6mmphi.
[0046] d. A sample with a width of face [of 5cm] and a die length of 15cm is used for the reinforcement of the separator of a separator on the strength, and it is JISL. According to 1068 (the tensile test approach of textiles), the tension rate was used as a part for 30cm/, having used grip spacing as 10cm, and the tensile strength in the direction of length (MD) was measured using the tensilon RTM-100 mold testing machine.
[0047] Example 1 polypropylene and SHINJI nerd theque polystyrene were extruded at the temperature of 295 degrees C by turns from the adjoining orifice. Solitary-foramen discharge quantity was taken as polypropylene =0.3g/min., and SHINJI nerd theque polystyrene =0.5g/min. 0.8 morekg/cm2 It was made to ******-ize by 300-degree C airstream, the bicomponent fiber (Chisso Corp., ES fiber, the diameter of fiber of 16 micrometers, die length of 50mm) of polypropylene/polyethylene was blown into coincidence, and three sorts of fiber created the nonwoven fabric by which homogeneity mixing was carried out. The heat press was carried out at 100 degrees C, and it considered as the thickness of 120 micrometers. The schematic diagram of a nonwoven fabric listing device was shown in drawing 1 . The above-mentioned sample is started in size with a width-of-face [of 10cm] x die length of 60cm, and it is SO3. With the nitrogen gas 10 volume % Containing gas, it carried out by processing for 30 seconds at the room temperature (25 degrees C). After processing permuted the reaction vessel with a lot of nitrogen gas, and suspended the sulfonation reaction. Used SO3 The Nisso ape fan by Nippon Soda Co., Ltd. was used for gas by evaporating with nitrogen gas. The used processor was shown in drawing 2 .
[0048] Using the created separator, nickel / hydrogen rechargeable battery of capacity 2500mAh were created, charge and discharge were repeated in 0.4C, and the discharge capacity maintenance factor was measured. Discharge capacity made 100% discharge capacity in the initial cycle after finishing 1 - 2 times of the preliminary charges and discharges for activation of a hydrogen storing metal alloy, and measured the maintenance factor of the discharge capacity when repeating a charge-and-discharge cycle. The potassium-hydroxide water solution was used for the electrolytic solution. The number of cycles when a discharge capacity maintenance factor falling to 50% was evaluated as a life of a cell.
[0049] The result of the life evaluation by the creation conditions, physical properties, and discharge capacity maintenance factor of a separator was summarized in Table 1.
[0050] Furthermore, for the check of the strength of sulfonation conditions, without using SHINJI nerd theque polystyrene, in the above-mentioned example 1, the nonwoven fabric with the equivalent diameter of fiber was created, and the tensile strength was measured only by the polyolefin fiber (T0). Furthermore, after carrying out sulfonation processing on the same sulfonation conditions as an example 1, the tensile strength was measured (T1). Here, the value calculated by (T1/T0) *100(%) was defined as polyolefine retention (%) on the strength, and was made into the scale of measurement of sulfonation conditions on the strength. The polyolefine retention on the strength in a result and an example 1 was 95% and a high value, its rate of sulfonation of a polyolefin fiber was small, and it was checked that polystyrene system super-thin fiber is sulfonated alternatively. Hereafter, in each example, the polyolefine retention on

the strength in each example is measured with the nonwoven fabric using the corresponding polyolefin fiber.
[0051] The mixed ratio, the diameter of fiber, and SO3 of the fiber used example 2-3 Except having changed the sulfonation time amount by gas, it is the approach of the same approach as an example 1, and separator creation and evaluation were carried out. The result of the life evaluation by the creation conditions, physical properties, and discharge capacity maintenance factor of a separator was summarized in Table 1.
[0052] Except having processed an example 4 - 5 sulfonation processing with the sulfuric acid, it is the same law as examples 1-2, and separator creation and evaluation were carried out. The result of the life evaluation by the creation conditions, physical properties, and discharge capacity maintenance factor of a separator was summarized in Table 1.
[0053] About the polyolefine 100% nonwoven fabric which does not contain example of comparison 1 ** sulfonation fiber, it is SO3. It processed at 110 degrees C by the oleum contained 15% of the weight, and the same measurement as an example 1 was carried out. They were a surface layer sulfur content and a value with strong insufficient both sides. The result was summarized in Table 2.
[0054] The polyolefine 100% nonwoven fabric which does not contain example of comparison 2 ** sulfonation fiber was processed on the same mild sulfonation conditions as an example 1. Although only the surface layer was sulfonated, the surface layer sulfur content was a low value, and solution retention of the result was not enough, and it was inadequate. [of the function as a separator] The result was summarized in Table 2.
[0055] Although spinning was carried out by the same melt blowing method as an example 1 using example of comparison 3 polypropylene, and SHINJI nerd theque polystyrene Although the entrainment of a bicomponent fiber evaluated by performing sulfonation processing for this nonwoven fabric that obtained the nonwoven fabric with a thickness of 120 micrometers with a 120-degree C heat press on the same sulfonation conditions as an example 1, and creating a separator after creating the nonwoven fabric, without carrying out Since air permeability was low, the balance of internal pressure collapsed in the charge-and-discharge cycle, and the extreme fall of a life occurred. The result was summarized in Table 2.
[0056]
[Table 1]

	実施例1	実施例2	実施例3	実施例4	実施例5
表面層硫黄含有量（元素%）	6．0	3．8	10．9	4．2	3．5
不織布組成 （含有率　重量%） ［繊維径　μm］	sPs(50)[7] PP(30)[5] PPE(20)[16]	sPs(35)[7] PP(30)[5] PPE(35)[16]	sPs(65)[2] PP(15)[5] PPE(20)[12]	sPs(50)[7] PP(30)[5] PPE(20)[16]	sPs(50)[10] PP(30)[8] PPE(20)[12]
スルホン化条件 （温度） （時間）	SO3ガス 25℃ 30秒	SO3ガス 25℃ 25秒	SO3ガス 25℃ 40秒	硫酸 60℃ 25分	硫酸 60℃ 16分
引っ張り強度（kgf／5cm幅）	10．0	10．8	11．9	9．4	8．0
目付（g／m²）	49	52	65	63	48
透気度（cc/cm2・s）	15．9	20．6	10．0	16．8	16．2
厚み（μm）	120	130	105	120	105
サイクル寿命（サイクル）	580	545	590	505	485
ポリオレフィン強度保持率(%)	95	95	92	86	89

sPs＝シンジオタクティクポリスチレン
PP＝ポリプロピレン
PPE＝ポリプロピレン／ポリエチレン（芯／鞘繊維）

[0057]
[Table 2]

	比較例１	比較例２	比較例３
表面層硫黄含有量（元素％）	２．２	０．９７	１．９
不織布組成 （含有率　重量％） ［繊維径　μｍ］	ＰＰ(50)［５］ ＰＰＥ(50)［10］	ＰＰ(50)［５］ ＰＰＥ(50)［10］	PP+sPs(85)［11］ ＰＰＥ(15)［16］
スルホン化条件 （温度） （時間）	発煙硫酸 １１０℃ ２５分	ＳＯ３ ｶﾞｽ ２５℃ ３０秒	ＳＯ３ ｶﾞｽ ２５℃ ３０秒
引っ張り強度（kgf／５cm幅）	６．９	１３．９	６．８
目付（ｇ／ｍ²）	４５	５２	４８
透気度（cc/cm2・s）	１６．８	１５．３	２９．８
厚み（μｍ）	１２０	１３０	１３０
サイクル寿命（ｻｲｸﾙ）	２９５	２５	２５０
ポリオレフィン強度保持率(%)	７０	９６	９７

ｓＰｓ＝シンジオタクティクティクポリスチレン
ＰＰ＝ポリプロピレン
ＰＰＥ＝ポリプロピレン／ポリエチレン（芯／鞘繊維）

[Translation done.]

* NOTICES.*

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the schematic diagram of a nonwoven fabric listing device.
[Drawing 2] SO3 It is the schematic diagram of the sulfonation processor by gas.

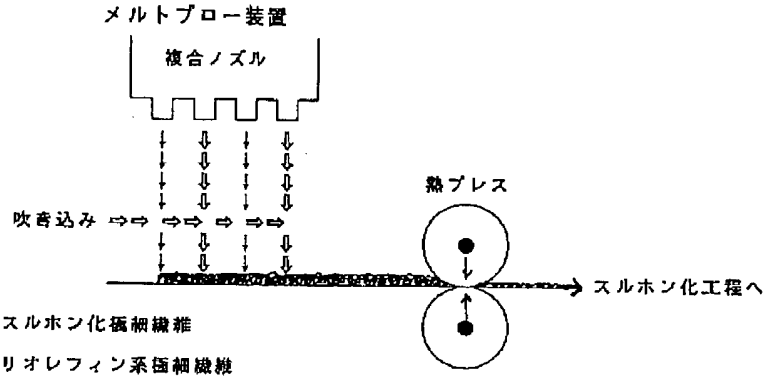
[Translation done.]

* NOTICES,*

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

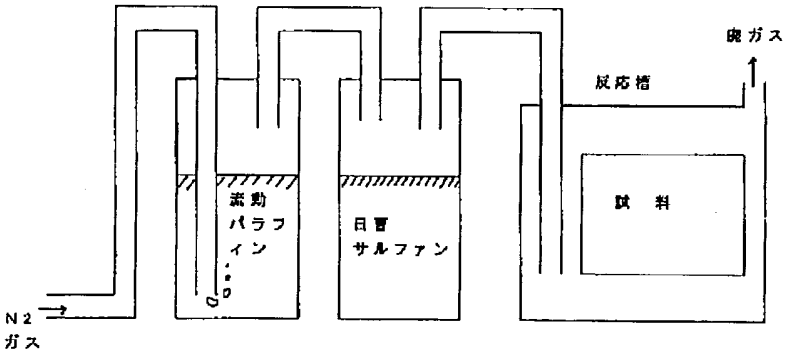
DRAWINGS

[Drawing 1]
不織布作成装置



↓：易スルホン化極細繊維
⇩：ポリオレフィン系極細繊維
⇨：繊維径が太いポリオレフィン系繊維

[Drawing 2]
スルホン化処理装置



[Translation done.]